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Sewage sludge torrefaction in a fluidized bed reactor

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HIGHLIGHTS

- Sewage sludge was torrefied in a fluidized bed reactor.
- The influence of torrefaction temperature on the products was determined.
- The influence of solid residence time on the products was determined.
- For short solid residence times, temperature over 270 °C is needed.

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ABSTRACT

Torrefaction of sewage sludge in a lab-scale fluidized bed reactor was studied in order to know if this pre-treatment could enhance the properties of this waste in subsequent thermochemical processing, such as pyrolysis. The influence was studied of two important torrefaction operational parameters, temperature (220–320 °C) and solid residence time (3.6–10.2 min), on the product distribution and properties. Taking into account the operation conditions evaluated in this work, torrefaction temperature affects solid product properties at long solid residence times (longer than 6.1 min) and that the effect of solid residence time is only significant at the highest temperature (320 °C). Severe torrefaction conditions result in the release of bonded water which could enhance some properties of the liquid obtained in the ensuing pyrolysis process. However, the torrefaction pre-treatment also implies that part of the extractives is lost from the raw material. Compared to dry raw sewage sludge, the energy density of sewage sludge after torrefaction increases under certain conditions. The removal of H_2O and CO_2 during the torrefaction step reduces the O/C ratio in the torrefied solid up to 0.12 (66.70% reduction compared to 0.37 in raw sewage sludge) which could be a benefit for subsequent thermochemical treatments. For example, one of the main drawbacks of pyrolysis liquids is their high oxygen content.

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1. Introduction

Reserves of fossil fuels have decreased in recent years and research into the production of fuel from biomass has been stepped up [1]. One of the materials which can be converted into fuel without competing with food production is sewage sludge (SS). SS is a waste generated from wastewater treatment plants. SS obtained during wastewater treatment has a high organic matter content (around 60–70% of dry matter if it is aerobically digested or around 40–50% of dry matter if it is anaerobically digested), nitrogen, phosphorous and potassium, but also heavy metals and organic pollutants [2].

The European legislation concerning the treatment of wastewater is becoming increasingly restrictive. Since the implementation of the Urban Waste Water Treatment Directive (UWWTD) (91/271/CEE) [3], the number of wastewater treatment plants installed has increased, and therefore the amount of SS generated has also increased. Nowadays, the management of SS is gaining importance. This waste has usually been incinerated, landfilled or used in agriculture. However, the application of SS to agricultural land may cause the transfer of contaminants (pathogens, viruses, heavy metals, polycyclic aromatic hydrocarbons and organochlorine residues) from SS to the soil, affecting microbial, plant and animal life [4,5]. There are other ways to manage this waste, including thermochemical treatments such as combustion, gasification and pyrolysis.

Thermochemical conversion technologies applied to biomass and also to sewage sludge (which could be considered a type of biomass) might have an important role in the production of energy. However, biomass may not be appropriate for energy production in its raw state. Sometimes, prior to thermochemical treatments, biomass is dried and chopped in order to have a solid with higher energy density, and to improve its handling characteristics. There are

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other options for biomass pre-treatment such as pelletisation, torrefaction and hydrothermal upgrading [6].

Torrefaction, also known as mild-pyrolysis, is a thermal treatment carried out at temperatures between 200 and 300 °C under atmospheric pressure conditions in the absence of oxygen [7,8]. It is applied as a pre-treatment for other thermal conversion techniques. The oxygen content of torrefied biomass is lower than the original biomass and the heating value is higher. During torrefaction, around 70% of the original material mass is preserved, which contains approximately 90% of the initial energy, so the energy density increases with torrefaction [8]. Some permanent and condensable gases are also formed during torrefaction reactions. This pre-treatment step favors subsequent thermochemical processes since grinding energy consumption and costs are lower for torrefied biomass than for fresh biomass, and the former is also more homogeneous [9,10].

Sewage sludge pyrolysis presents some problems which could be mitigated by means of torrefaction pre-treatment, owing to the characteristics that biomass acquires after torrefaction. Pyrolysis liquid from sewage sludge has high water and oxygen contents, which are not appropriate for the use of this liquid as fuel. High liquid water content leads to liquid instability and decreases the heating value [11].

In the case of biomass gasification, pre-treatment of the raw material is required in order to achieve an easier biomass feeding into the gasifier, reduce transport costs and improve the gasifier operation (if biomass energy density is increased a smaller gasifier is required). In order to avoid the decrease in total gasification efficiencies when torrefaction pre-treatment is carried out, torrefaction gases should be used in the process as gasification agent [12]. Torrefied biomass loses resilient and fibrous properties, and it can be easily milled. Besides, the high porosity of torrefied biomass increases its reactivity during gasification [13,14]. Gasification of torrefied wood produces the same quantity of CO_2 but more H_2 and CO than gasification of the parent wood, due to the increase in the C and H contents in torrefied wood [15].

There are several works about torrefaction of lignocellulosic biomass [13–20] but torrefaction of non-lignocellulosic biomass, such as SS, has been studied to a lesser extent. Dhungana et al. [21] studied sewage sludge torrefaction in a muffle furnace. They determined the final solid yield and the energy yield of torrefaction under specific conditions of temperature (250–280 °C) and solid residence time (15–60 min). These authors found out that, although sewage sludge is low or free from hemicellulose, the energy density of the solid increased with torrefaction, and that the torrefaction temperature had a greater effect on torrefaction than the solid residence time. Ábrego et al. [22] proposed a three-stage thermochemical process for the valorization of sewage sludge, in which the first stage was torrefaction. Torrefaction was studied first in a fixed bed reactor in order to optimize the operating conditions. Afterwards, torrefaction was also tested in a fluidized bed reactor. Regarding the experimental system, a variety of set-ups has been used for biomass torrefaction, with quartz tube reactors, thermogravimetric analyzers and rotary kilns being the most common. Li et al. [18] used a fluidized bed reactor for sawdust torrefaction given the energy efficiency improvement and the shorter reaction time. There are some studies in the literature in which quite short residence times have been used. Repellin et al. [23] recommend solid residence times lower than 20 min since the anhydrous weight loss occurs primarily during the first 20 min. Besides, these authors also point out that short reaction times are more suitable for industrial applications. Ren et al. [24] studied a reaction time range of 8–20 min, Prins et al. [25] used torrefaction times of 10 and 15 min, and Medic et al. [9] also used solid residence time of 10 min.

The effect of the operational conditions of SS torrefaction on the properties of the products obtained is investigated in the present work. Different torrefaction temperatures and solid residence times were tested in a lab-scale fluidized bed reactor. The study was focused on the properties of the torrefied solid product obtained, given the potential application of this product in thermochemical processes.

2. Material and methods

2.1. Raw material

An anaerobically digested and thermally dried SS, from a Spanish wastewater treatment plant, was utilized in this study. The proximate and ultimate analysis, higher heating value (wet SS basis), density and energy density of this material are listed in Table 1. The bulk density of the sewage sludge was obtained by a non-standardized method. A known volume (25 mL) of sewage sludge was weighed and the density was calculated. Sewage sludge was compacted until the height of the bed did not change. The energy density results from the multiplication of density by higher heating value.

The organic extractives content (the most non-polar compounds of SS, such as fatty acids or phenolics [26]) was determined by Soxhlet extraction with *n*-hexane followed by dichloromethane extraction. The extractives content was 4.50 wt.% (as received). The composition of SS extractives was analyzed by GC–MS. The compounds found in the extractives were aliphatic hydrocarbons, fatty acids, compounds derived from benzene, steroids and sterols.

2.2. Experimental system

A laboratory-scale (<1 kg h^{-1}) fluidized bed was used to carry out the SS torrefaction experiments. The layout of the plant is shown elsewhere [27].

The reactor operated at atmospheric pressure, with continuous solid feed and continuous removal of solid product. The fluidizing gas was nitrogen and a volumetric flow of 0.074 m^3 (STP) m^{-2} s^{-1} was introduced.

The solid bed consisted of solid product from SS torrefaction previous experiments, in order to reduce the problems associated to the start-up period [28,29]. The amount of bed material introduced is around 40 g in all cases. The maximum height that the bed can reach is 150 mm, since there is an overflow at this height. SS was ground, sieved (250–500 μm) and fed to the reactor by a variable-speed screw feeder at a feed rate between 6.0 and 16.0 g min^{-1}. The solid feed rate during torrefaction was one of the experimental variables studied in this work and is directly re-

Table 1
Proximate and ultimate analysis of the raw material.

	Analytical standard	Units	SS
Moisture	ISO-589-1981	wt.%	6.48
Ash	ISO-1171-1976	wt.%	39.04
Volatiles	ISO-5623-1974	wt.%	50.09
Fixed carbon	[a]	wt.%	4.40
Carbon	[b]	wt.%	29.50
Hydrogen[c]	[b]	wt.%	4.67
Nitrogen	[b]	wt.%	5.27
Sulfur	[b]	wt.%	1.31
Oxygen	[d]	wt.%	20.20

[a] By difference.
[b] Ultimate analysis was performed using Carlo Erba 1108.
[c] The wt.% of hydrogen includes hydrogen from the moisture.
[d] oxygen (wt.%) = 100 – carbon (wt.%) – hydrogen (wt.%) – nitrogen (wt.%) – sulfur (wt.%) – ash (wt.%).

lated to solid residence time. Solid residence time was calculated as the ratio between the mass of torrefied sewage sludge remaining in the bed after the experiment and the flow of sewage sludge introduced during the experiment. The value of this variable is not controllable directly by the operator because, in addition to its dependence on the solid feed rate, it slightly depends on the temperature. The average solid residence time varies from 3.6 to 10.2 min in this work and the average experiment run time is around 100 min. The extractives content (Ext_{cont}), ultimate analysis, density (ρ_{TSS}) and higher heating value (HHV_{TSS}) of the torrefied sewage sludge (TSS) were determined with the same methods as those used for raw sewage sludge (see Section 2.1). For each experiment, the ultimate analysis was measured once while the higher heating value and the bulk density were measured three times, and the extractives content was measured twice. The energy density (ρ_{ener}) of torrefied sewage sludge was also calculated.

The bed and the freeboard of the reactor, and the cyclone were heated by an electrical furnace. The torrefaction temperature was the other experimental condition studied. This was varied between 220 and 320 °C. The freeboard and the cyclone temperatures were set at the same temperature as the bed reactor.

A hot filter was placed before the condensation system in order to retain the smaller solid particles. The temperature of the hot filter was the same as the bed reactor temperature. The gas residence time varied from 6.17 s at 220 °C to 5.02 s at 320 °C. This residence time was calculated as the ratio between the volume of the reactor (bed volume plus freeboard volume) and the volumetric flow of the flue noncondensable gases (NCG). The condensation system for the liquid product, placed after the hot filter, was composed of two ice-cooled condensers and one electrostatic precipitator. Water and organic compounds condensed in this system and the exiting gas flow consisted of non-condensable gases (NCG). A micro-gas chromatograph (micro-GC; Agilent 3000A) was used to determine composition of the exit gas. Specifically, the analyzed gases were CO_2, CO, H_2, CH_4, C_2H_2, C_2H_4, C_2H_6 and H_2S. The experimental procedure carried out is explained elsewhere in great detail [27].

The liquid fractions were stored in a fridge at 3–5 °C until they were analyzed. The water content (W) of these liquids was analyzed by the Karl-Fischer titration method. These data, together with the liquid yield, allowed us to calculate the yield to water with respect to the SS introduced in each experiment. The water yield was calculated as the ratio between the amount of water obtained and the amount of raw SS fed in each experiment. The yield to organic compounds was calculated as the difference between the liquid yield and the water yield. A qualitative analysis of the organic compounds present in the condensed fractions was performed by gas chromatography and mass spectrometry (GC–MS; Agilent 7890A).

Table 2
Response variables studied.

Variable	Product	Nomenclature	Units
Torrefied SS yield	Solid	η_{TSS}	wt.%
O/C molar ratio	Solid	O/C	
H/C molar ratio	Solid	H/C	
Higher heating value	Solid	HHV_{TSS}	MJ kg^{-1}
Higher heating value (daf)	Solid	HHV_{TSS} (daf)	MJ kg^{-1}
Energy density	Solid	$\rho_{ener,TSS}$	MJ dm^{-3}
Energy yield	Solid	η_{energy}	%
Extractives content	Solid	$Ext_{cont,TSS}$	wt.%
Extractives yield	Solid	$\eta_{extractives}$	wt.%
Sulfur removal	Solid	$S_{removal}$	wt.%
Sulfur content (daf)	Solid	$S_{cont,TSS}$ (daf)	wt.%
Condensables yield	Liquid	η_{cond}	wt.%
Water yield	Liquid	η_{water}	wt.%
Organic compounds yield	Liquid	$\eta_{organic}$	wt.%
Permanent gases yield	Gas	η_{gas}	wt.%
CO_2 yield	Gas	η_{CO2}	wt.%
H_2S yield	Gas	η_{H2S}	wt.%

Besides torrefaction runs in the fluidized bed reactor, thermogravimetric (TGA) analyses were carried out using a NETZSCH STA 449 Jupiter® thermobalance. TGA torrefaction experiments for the study were performed under an inert atmosphere using nitrogen as carrier gas with a flow rate of 250 mL min^{-1}. A small quantity of sewage sludge (around 5 mg) was heated at 10 °C min^{-1} from 35 °C to the desired temperature (220, 270 and 320 °C) and maintained at this temperature until reaching constant weight.

2.3. Experimental design

A Central Composite Design (CCD) was used to study the influence of two important torrefaction parameters (temperature and solid residence time) on torrefaction products, especially on the properties of the solid product. This design consisted of a Full Factorial Design (FFD) of two factors and two levels (4 runs), 3 center runs and 4 axial runs. Therefore, 11 runs were performed. The factors evaluated were bed temperature and solid feed rate. Solid feed

Table 3
Design matrix and mass balance.

	Average residence time (min)											
	3.6	6.1	10.2	3.6	6.1	10.2	3.6	6.1	10.2	3.6	6.1	10.2
Temperature (°C)	**Residence time (min)**			**η_{TSS} (daf) (wt. %)**			**η_{cond} (daf) (wt. %)**			**η_{gas} (daf) (wt. %)**		
220	3.6	6.3	10.8	91	95	96	2	1	1	0.04[b]	0.05	0.16
270	4.1	6.5 ± 0.2[a]	9.1	91	91 ± 1[a]	90	1	2 ± 1[a]	3	0.10	0.20 ± 0.04[a]	0.42
320	3.0	4.6	10.7	86	62	55	6	27	30	1.05	5.34	5.01
Coefficient of Variation[c] (%)	4			1			69			22		
Temperature (°C)	**η_{TSS} (wt. %)**			**η_{cond} (wt. %)**			**η_{gas} (wt. %)**			**Mass balance (wt. %)**		
220	94.8	95.5	94.9	7.6	4.4	6.6	0.02[b]	0.03	0.09	102.4	99.9	101.6
270	93.5	92.4 ± 1.2[a]	90.6	5.6	7.0 ± 1.1[a]	8.2	0.06	0.11 ± 0.02[a]	0.23	99.2	99.5 ± 0.5[a]	99.0
320	88.4	73.9	71.3	9.7	21.4	22.3	0.57	2.91	2.73	98.7	98.2	96.3
Coefficient of Variation[c] (%)	1			16			22			1		

[a] Mean value ± standard deviation of the results obtained at the center point conditions.

[b] Under detection precision.

[c] Calculated from the results obtained for the different response variables at the center point conditions.

rate was chosen as a factor instead of solid residence time because it is completely independent from torrefaction temperature. As mentioned before, solid residence time could be affected by the bed temperature and the design of experiments requires that the factors studied are completely independent. The bed temperature (T) range was 220–320 °C and the solid feed rates (Q_{feed}) used were 6, 11 and 16 g min^{-1}, which resulted in solid residence times, expressed as average ± standard deviation, of 10.2 ± 0.9, 6.1 ± 0.9 and 3.6 ± 0.5 min, respectively. The response variables studied were those listed in Table 2.

The experimental conditions of all the experiments performed are shown in Table 3. The experimental data were analyzed through analysis of variance (ANOVA) with a confidence level of 95%. The replicates of the center point (270 °C and 11 g min^{-1}) are useful in order to evaluate the experimental error and the curvature. The CCD was used because most of the response variables did not follow a linear trend with the factors within the range of study. The CCD allowed the fitting of second-order models [30]. Therefore, the data were used in building second-order response surface models. The model coefficients allow the determination of the relative influence of each torrefaction parameter evaluated (factor) on the variable. The higher the coefficient is, the higher the factor effect. For each one of the response variables, the plots represented and the discussion of the results are based on the values calculated from the models obtained.

Table 4
Experimental results.

	Average residence time (min)								
	3.6	6.1	10.2	3.6	6.1	10.2	3.6	6.1	10.2
Temperature (°C)		O/C			H/C			HHV$_{TSS}$ (MJ·kg^{-1})	
220	0.31	0.38	0.33	1.67	1.70	1.76	13.02	13.08	12.90
270	0.35	0.36 ± 0.00[a,d]	0.32	1.36	1.68 ± 0.04[a,d]	1.66	13.04	13.30 ± 0.08[a]	13.49
320	0.32	0.16	0.12	1.66	1.29	1.19	13.62	13.25	12.05
Raw SS		0.37			1.59			12.79	
Coefficient of Variation[c] (%)		0.00			3			0.6	
Temperature (°C)		HHV$_{TSS}$ (daf) (MJ·kg^{-1})			ρ_{TSS} (kg·dm^{-3})			ρ_{ener} (MJ·dm^{-3})	
220	25.0	24.0	23.4	0.880	0.862	0.872	11.5	11.3	11.3
270	24.5	24.9 ± 0.1[a]	25.1	0.873	0.877 ± 0.004[a]	0.865	11.4	11.6 ± 0.2[a]	11.7
320	25.6	29.2	28.7	0.848	0.792	0.802	11.5	10.6	9.7
Raw SS		23.5			0.862			11.02	
Coefficient of Variation[c] (%)		0.5			0.4			1	
Temperature (°C)		η_{energy} (%)			Ext$_{cont,TSS}$ (wt. %)			$\eta_{extractives}$ (wt. %)	
220	96.4	97.6	95.8	3.3	2.8	3.4	70	60	71
270	95.3	96.0 ± 0.8[a]	95.6	3.0	3.0 ± 0.1[a]	3.1	63	62 ± 3[a]	62
320	94.1	77.7	66.7	2.2	2.2	0.6	43	36	9
Raw SS		-			4.5			-	
Coefficient of Variation[c] (%)		0.8			4			6	
Temperature (°C)		S$_{removal}$ (wt. %)			S$_{cont,TSS}$ (wt. %)			W (wt. %)	
220	22	18	20	2.06	2.07	2.02	94	93	95
270	26	29 ± 4[a,d]	29	1.94	1.95 ± 0.08[a,d]	1.90	94	93 ± 2[a]	99
320	24	65	67	2.12	1.38	1.47	91	75	67
Raw SS		-			1.31			-	
Coefficient of Variation[c] (%)		15			4			2	
Temperature (°C)		η_{water} (wt. %)			$\eta_{organic}$ (wt. %)			η_{CO2} (wt. %)	
220	7.1	4.1	6.2	0.5	0.3	0.4	0.02[b]	0.03	0.09
270	5.2	6.5 ± 0.8[a]	8.1	0.3	0.5 ± 0.2[a]	0.1[b]	0.05	0.09 ± 0.02[a]	0.16
320	8.8	16.0	15.1	0.9	5.4	7.6	0.51	2.51	2.27
Coefficient of Variation[c] (%)		13			45			22	
Temperature (°C)		η_{H2S} (wt. %)							
220	0.002[b]	0.000[b]	0.000[b]						
270	0.006	0.012 ± 0.005[a]	0.045						
320	0.059	0.277	0.278						
Coefficient of Variation[c] (%)		40							

[a] Mean value ± standard deviation of the results obtained at the center point conditions.
[b] Under detection precision.
[c] Calculated from the results obtained for the different response variables at the center point conditions.
[d] Determined for only two replicates.

Table 5

Coefficients of the terms of the coded model of the factorial design for the response variables.

	Response variable	Independent term	T	Q_{feed}	$T \cdot Q_{feed}$	T^2	Q_{feed}^2	$T^2 \cdot Q_{feed}$	$T \cdot Q_{feed}^2$	R^2[a]
Product distribution	η_{TSS} (wt.%)	92.1 ± 2.6	−8.6 ± 2.3	n.s[b]	4.3 ± 2.9	−5.9 ± 3.5	n.s[b]	4.2 ± 2.9	n.s[b]	0.96[c]
	η_{cond} (wt.%)	7.0 ± 1.7	8.5 ± 2.6	n.s[b]	−3.4 ± 1.8	5.1 ± 2.2	n.s[b]	−2.9 ± 1.8	−4.0 ± 3.2	0.98[c]
	η_{gas} (wt.%)	0.27 ± 0.05	1.44 ± 0.07	−0.09 ± 0.07	−0.52 ± 0.05	1.04 ± 0.07	−0.29 ± 0.06	−0.47 ± 0.09	−0.64 ± 0.09	0.99[c]
Product distribution (daf)	η_{TSS} (daf) (wt.%)	91 ± 2	−17 ± 3	n.s[b]	9 ± 2	−10 ± 2	n.s[b]	7 ± 2	5 ± 3	0.99[c]
	η_{cond} (daf) (wt.%)	2 ± 2	n.s[b]	13 ± 4	−6 ± 3	10 ± 3	n.s[b]	−6 ± 3	−5 ± 5	0.99[c]
	η_{gas} (daf) (wt.%)	0.50 ± 0.10	2.65 ± 0.14	−0.16 ± 0.13	−0.96 ± 0.09	1.90 ± 0.12	−0.53 ± 0.12	−0.86 ± 0.16	−1.18 ± 0.16	0.99[c]
Solid	HHV_{TSS} ($MJ \cdot kg^{-1}$)	13.30 ± 0.21	n.s[b]	n.s[b]	0.36 ± 0.22	−0.29 ± 0.27	n.s[b]	0.42 ± 0.22	n.s[b]	0.89[c]
	HHV_{TSS} (daf) ($MJ \cdot kg^{-1}$)	25.1 ± 0.2	2.6 ± 0.2	−0.4 ± 0.1	−1.2 ± 0.2	1.3 ± 0.2	−0.5 ± 0.2	n.s[b]	−1.1 ± 0.3	0.99[c]
	ρ_{ener} ($MJ \cdot dm^{-3}$)	11.6 ± 0.2	−0.4 ± 0.1	n.s[b]	0.4 ± 0.2	−0.6 ± 0.2	n.s[b]	0.5 ± 0.2	n.s[b]	0.97[c]
	η_{energy} (%)	95.7 ± 0.7	−9.9 ± 1.1	n.s[b]	6.7 ± 0.8	−7.8 ± 0.9	n.s[b]	7.0 ± 0.8	2.1 ± 1.3	0.99[c]
	$\eta_{extractives}$ (wt.%)	62 ± 8	−12 ± 7	n.s[b]	9 ± 9	−14 ± 11	n.s[b]	8 ± 9	−10 ± 9	0.99[c]
Liquid	η_{water} (wt.%)	6.6 ± 0.8	5.9 ± 1.2	−1.4 ± 0.7	−1.8 ± 0.9	3.0 ± 1.1	n.s[b]	n.s[b]	−3.3 ± 1.5	0.99[c]
Gas	η_{CO2} (wt.%)	0.23 ± 0.08	1.24 ± 0.11	n.s[b]	−0.42 ± 0.08	0.90 ± 0.10	−0.27 ± 0.10	−0.46 ± 0.08	−0.57 ± 0.13	0.99[c]
	η_{H2S} (wt.%)	0.029 ± 0.011	0.140 ± 0.015	−0.020 ± 0.015	−0.055 ± 0.011	0.093 ± 0.016	−0.020 ± 0.013	−0.035 ± 0.019	−0.055 ± 0.019	0.99[c]

[a] Coefficient of regression, defined as the ratio between the sum of squares explained by the model and the total sum of squares.

[b] Not significant term (*p*-value <0.05).

[c] Lack of fit not significant (*p*-value >0.05).

In some cases it was interesting to compare the properties of raw sewage sludge and torrefied sewage sludge. In this case a one-way analysis of variance (one-way ANOVA) was applied, at a confidence level of 95%. A multiple range test, the Least Significance Difference (LSD) test was used to compare pairs of values.

3. Results and discussion

All the experimental results are displayed in Tables 3 and 4. To evaluate the reproducibility of the experimental system, Tables 3 and 4 also contain the mean value, the standard deviation and the coefficient of variation of the results obtained for the different response variables in the center point experiments. Mass balance closures are over 95 wt.%. The yield to organic compounds shows a high coefficient of variation (45%). The small amount of organic compounds generated makes it difficult to quantify them.

Table 5 displays the model coefficients for all the response variables analyzed in this work. As commented in the Material and Methods subsection, the higher the coefficient is, the higher the influence of the term. Moreover, the sign of the coefficient indicates whether the response variable increases (+) or decreases (−) when a linear term augments or if there is a maximum (−) or a minimum (+) according to the sign of the quadratic terms.

3.1. Thermogravimetric results

Fig. 1 displays TGA isothermal plots at different torrefaction temperatures. It shows trends of mass change during torrefaction of sewage sludge. SS heated to 220, 270 and 320 °C retains 85%, 73% and 67% of the weight of the initial material, respectively. The loss of mass greatly exceeded the initial value of the sewage sludge moisture. This means that the decomposition of organic matter in sewage sludge is substantial.

3.2. Product distribution

The yields obtained for each one of the torrefaction products and compounds are expressed per unit mass of feedstock. They are defined as the percentage ratio between the weight of the product (or compound) after torrefaction experiments and the weight of raw sewage sludge fed. The results obtained, as well as the mass balances, are shown in Table 3. Temperature exerts more influence than solid residence time on the product distribution (evidenced by its higher coefficient values), as occurred in the study developed by Dhungana et al. [21].

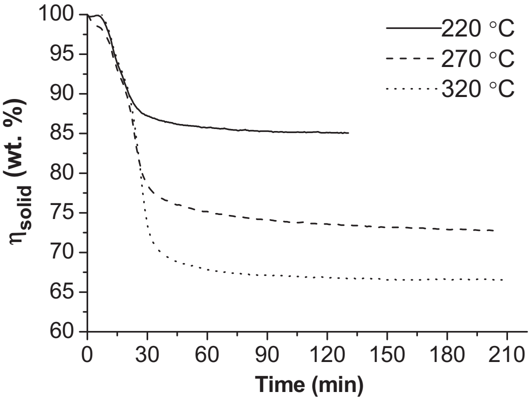


Fig. 1. Thermogravimetric analysis for sewage sludge.

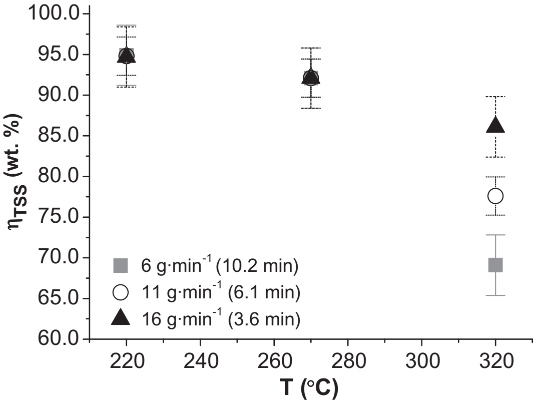


Fig. 2. Torrefied sewage sludge yield vs. temperature for different solid feed rate values. The results are expressed as the model value at each torrefaction condition ±0.5·Fisher LSD interval (taking into account all the runs).

3.2.1. TSS yield

Depending on the torrefaction parameters, the yield to torrefied SS (η_{TSS}) varies between 69.1 ± 3.7 and 94.9 ± 3.7 wt.%. The plot of the solid product yield versus bed temperature for different solid feed rates is shown in Fig. 2.

The torrefied sewage sludge yield decreases with the increasing temperature (negative model coefficient). However, as interaction between both factors is significant, the effect of the torrefaction temperature depends on the value of solid residence time. Taking into account the solid residence range studied, the mass of torrefied solid obtained decreases as the temperature increases from 270 °C to 320 °C, except at the shortest residence time. At 320 °C the TSS yield is higher for the shortest solid residence time (3.6 min). The bed temperature is the most influential parameter on the TSS yield (highest model coefficient).

When compared with the results obtained in the thermogravimetric analyses, the yields to solid product are similar for similar solid residence times, but higher than those obtained at longer residence times in the thermobalance. This may mean that sewage sludge would react to a greater extent at longer residence times in the fluidized bed reactor.

3.2.2. Condensables and gas yields

The condensables yield (η_{cond}) varies between 3.6 ± 2.1 and 22.9 ± 2.5 wt.%, and the permanent gas yield (η_{gas}) between 0.00 ± 0.06 and 2.90 ± 0.05 wt.%. Fig. 3 shows the yield to liquid product versus bed temperature and solid feed rate. As the gas

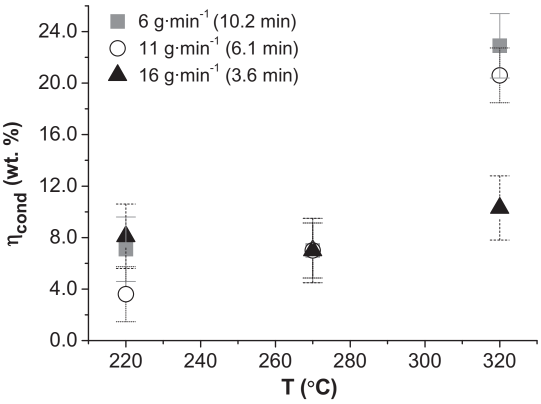


Fig. 3. Condensables yield vs. temperature for different solid feed rate values. The results are expressed as the model value at each torrefaction condition ±0.5·Fisher LSD interval (taking into account all the runs).

yield shows a similar trend to the condensables yield, Fig. 3 also explains the gas yield behavior within the range of study.

Temperature affects the yield to liquid and gas products to a large extent. Both yields increase with the increasing temperature. The trend of the liquid and gas yields is in accordance with the TSS yield variation. The yields increase with temperature for a residence time higher than 6.1 min, especially from 270 to 320 °C. The solid residence time affects the liquid and gas yields at 320 °C, obtaining higher yields at the longer residence times (6.1 and 10.2 min). More devolatilization reactions take place and the velocity of these reactions is higher at the higher temperatures, but a solid residence time of at least 6.1 min is required to notice the temperature effect on the products yields.

3.3. TSS properties

The TSS properties analyzed were ultimate analysis, higher heating value (HHV_{TSS}), higher heating value (daf) (HHV_{TSS} (daf)), energy density (ρ_{ener}), energy yield (η_{energy}), extractives yield ($\eta_{extractives}$) and sulfur removal ($S_{removal}$). Table 4 shows the experimental results obtained for these properties. The main results of the ANOVA analysis are shown in Table 5.

3.3.1. Ultimate analysis

A Van Krevelen diagram for the torrefied solids and the raw SS is presented in Fig. 4. Both the O/C and H/C molar ratios were calculated on a dry matter basis. As can be observed in Fig. 4, torrefaction provokes a decrease in the O/C ratio in most cases due to the loss of carbon in the form of carbon dioxide and light hydrocarbons. In some cases the H/C ratio increases, compared to raw SS, due to the fact that, although hydrogen is lost mainly in the form of water, the loss of carbon is proportionally higher than the loss of hydrogen.

3.3.2. Higher heating value

The higher heating value of torrefied SS varies from 12.23 ± 0.26 to 13.79 ± 0.26 MJ kg^{-1} within the range of study. Torrefied sewage sludge has lower moisture content than raw sewage sludge. Therefore, the daf (dry, ash free) higher heating value was calculated in order to study the real effect of torrefaction on the higher heating value of the solid, without taking into account the drying of the material and its final ash content. The effects of the torrefaction temperature and SS feed rate on the torrefied SS higher heating value (daf) are shown in Fig. 5. This response variable ranges from 23.6 ± 0.2 to 29.0 ± 0.2 MJ kg^{-1}.

The most influential operational condition within the range of study is the temperature which shows the biggest coefficient value, as can be observed in Table 5. The TSS HHV (daf) increases with the temperature especially from 270 to 320 °C and for a longer solid residence time (6.1 and 10.2 min). The effect of the solid residence times studied could begin to be noticed at 270 °C. A longer solid residence time (10.2 min) permits more decarboxylation reactions

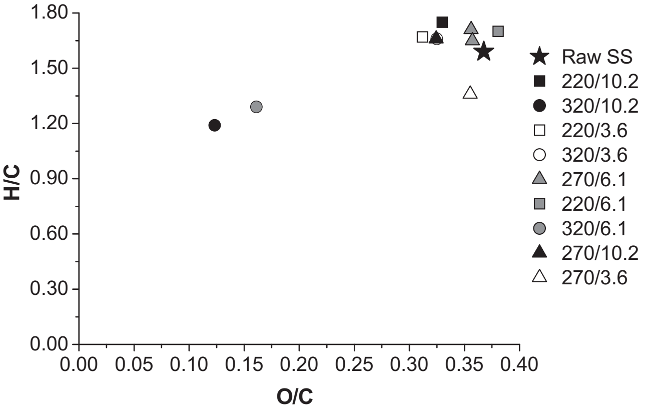


Fig. 4. Van Krevelen diagram for raw SS and TSS. The points corresponding to TSS are indicated with temperature/solid feed rate label in the legend chart.

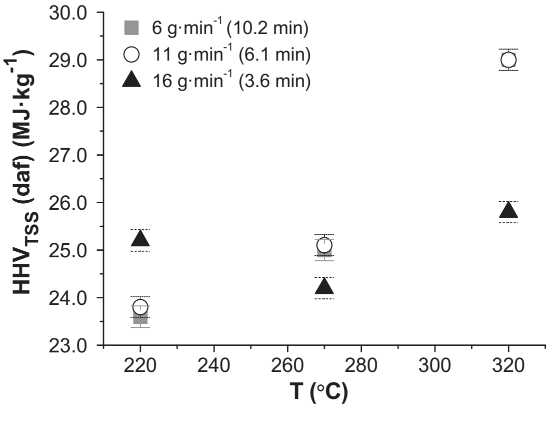


Fig. 5. Torrefied sewage sludge higher heating value (daf) vs. temperature for different solid feed rate values. The results are expressed as the model value at each torrefaction condition ±0.5·Fisher LSD interval (taking into account all the runs).

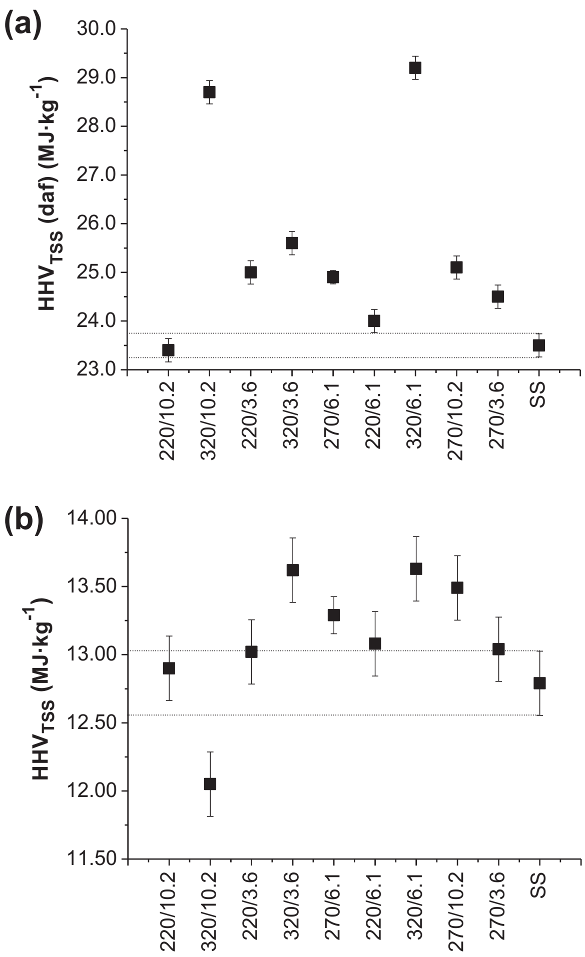


Fig. 6. (a) Comparison of raw SS HHV (daf) and torrefied SS HHV (daf) (LSD interval). (b) Comparison of raw SS HHV and torrefied SS HHV (LSD interval).

to develop at that temperature provoking a slight increase in the TSS HHV (daf). In these cases, torrefied sewage sludge retains compounds with higher energy content than the compounds that are released.

In order to determine whether the HHV of TSS is significantly different from that of raw SS, a one-way ANOVA analysis followed by a Least Significant Difference test (95% confidence level) was carried out. The comparison is represented in Fig. 6.

The one-way ANOVA and LSD test (95%), represented in Fig. 6a, reveals that only the higher heating value (daf) of torrefied SS at 220 °C and 10.2 min is not significantly different to the higher heating value (daf) of raw SS. The rest of the operational conditions give rise to solids with higher HHV (daf) than raw SS, especially when the SS was torrefied at a high temperature (320 °C) and a high solid residence time (6.1 and 10.2 min). Under these conditions, torrefied sewage sludge shows a rise in HHV (daf) of 24.3 and 22.1%, respectively. As can be observed in Fig. 6b, torrefaction at 220 °C does not provoke any changes in HHV with respect to the sewage sludge HHV. This is also the case with torrefaction at 270 °C and the shortest residence time (3.6 min). Torrefied sewage sludge obtained under the most severe conditions shows lower HHV. The rest of the torrefaction conditions generated torrefied sewage sludge with higher HHV than the raw SS.

3.3.3. Energy density

Fig. 7a shows the changes in energy density of torrefied sewage sludge with the different operational conditions within the range of study. Temperature affects the energy density for the long residence times studied (over 6.1 min). The energy density of torrefied sewage sludge using solid residence times of 6.1 or 10.2 min significantly decreases at 320 °C, the longer the residence time, the lower the energy density. This can be explained because these conditions lead to bulk density decrease, and therefore energy density decreases. At the most severe conditions used in this work (320 °C and 10.2 min) the decrease in energy density is far higher because the HHV of the solid is lower due to the fact that the mass loss entails the increase in the ash concentration of the material. At temperatures lower than 270 °C, the effect of solid residence time is not significant.

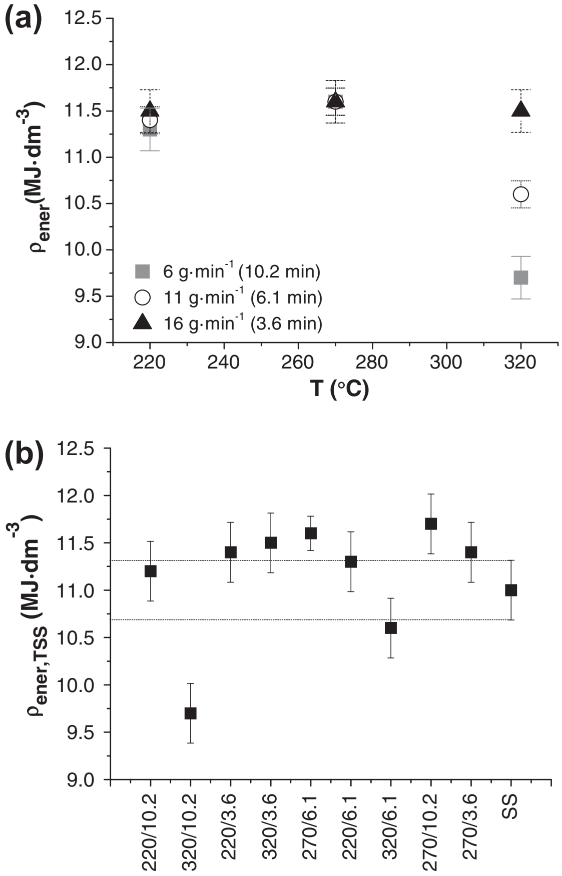


Fig. 7. (a) Torrefied sewage sludge energy density vs. temperature for different solid feed rate values. The results are expressed as the model value at each torrefaction condition ±0.5·Fisher LSD interval (taking into account all the runs). (b) Comparison of SS energy density and torrefied SS energy density (LSD interval).

Energy density of raw SS is only improved by torrefaction at 270 °C and solid residence times of 6.1 and 10.2 min, as the LSD 95% test indicates. Fig. 7b shows these results. In both cases, the increase in energy density is around 6%, which is similar to the results obtained by Dhungana et al. [21] (7% for digested SS torrefaction at 250 °C and at 30 min residence time).

3.3.4. Energy yield

The energy yield, on dry, ash free basis (daf), indicates the energy content of raw sewage sludge retained in the torrefied solid [21]. This was calculated using the following equation.

$$\eta_{\text{energy}}(\%) = \frac{\eta_{\text{TSS}}(\text{daf})\cdot \text{HHV}_{\text{TSS}}(\text{daf})}{\text{HHV}_{\text{SS}}(\text{daf})} \qquad (1)$$

The energy yield varied from 66.4 ± 1.0 to 97.8 ± 0.9% within the range of study. The work carried out by Dhungana et al. showed that digested SS retained between 84% and 99% of the initial energy content, within their range of study (250–280 °C, 15–60 min). It can be seen in Fig. 8 that the most significant differences regarding the energy yield are achieved at 320 °C. At this temperature, taking into account the solid residence times studied, the higher the solid residence time, the lower the energy yield reached. If the solid residence time is long enough, SS decomposition takes place to a large extent and thus the energy yield decreases. The energy yield is over 90% for torrefaction at 220 and 270 °C, regardless of the solid residence time, and at 320 °C with a solid residence time of 3.6 min.

3.3.5. Extractives yield

In view of the possible applications of TSS, it is desirable that the solid product retains most of the extractive compounds of the starting material. The yield to extractives was analyzed, defined as the percentage ratio between the amount of extractives

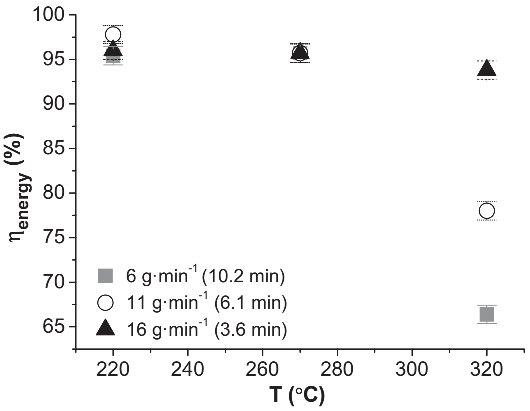


Fig. 8. Energy yield vs. temperature for different solid feed rate values. The results are expressed as the model value at each torrefaction condition ±0.5·Fisher LSD interval (taking into account all the runs).

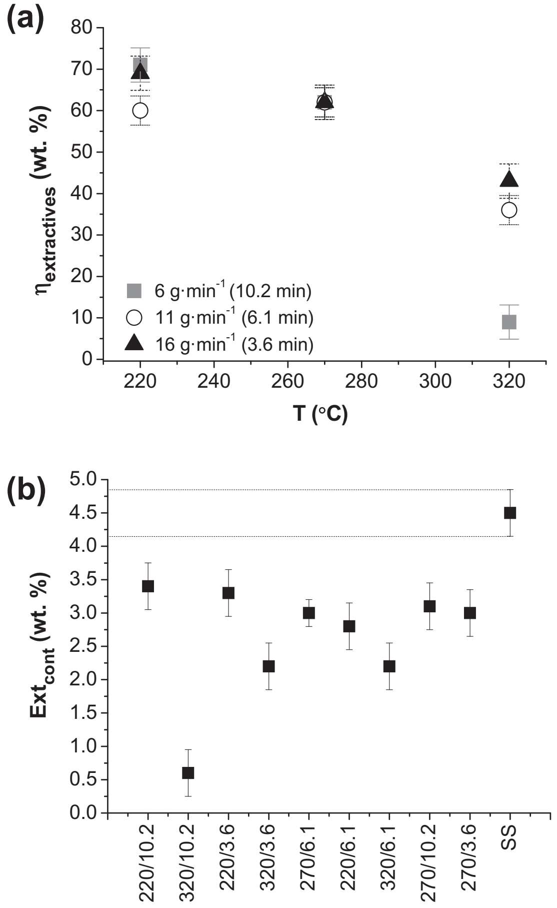


Fig. 9. (a) Extractives yield vs. temperature for different solid feed rate values. The results are expressed as the model value at each torrefaction condition ±0.5·Fisher LSD interval (taking into account all the runs). (b) Comparison of SS extractives content and torrefied SS extractives content (LSD interval).

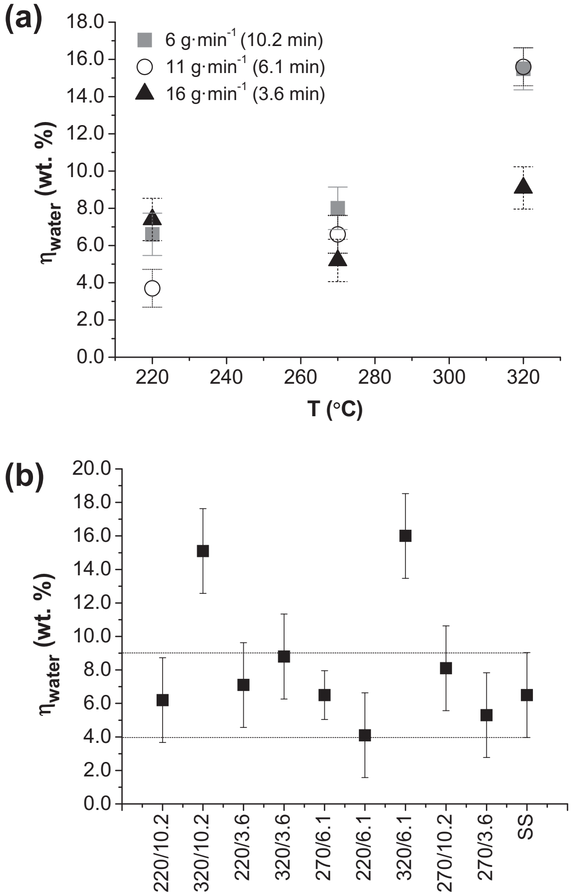


Fig. 10. (a) Water yield vs. temperature for different solid feed rate values. The results are expressed as the model value at each torrefaction condition ±0.5·Fisher LSD interval (taking into account all the runs). (b) Comparison of SS water content and water yield (LSD interval).

in TSS and the amount of extractives in raw SS. This response variable varies between 9 ± 4 and 71 ± 4 wt.%. The variation in the extractives yield with T and Q_{feed} is shown in Fig. 9a.

The torrefaction temperature has a significant effect on the extractives yield at each one of the solid residence times studied, especially when the temperature increases from 270 to 320 °C. The solid residence time has a significant effect on the extractives yield when torrefaction is carried out at 320 °C. The yield decreases from 43 ± 4 to 9 ± 4 wt.% while increasing the solid residence time from 3.6 to 6.1 min. These trends can also be explained by kinetics. At long solid residence times, devolatilization reactions of the extractives take place to a great extent. These reactions are also favored by increasing temperature. The bed temperature is the most influential parameter as can be observed in Table 5. Fig. 9b displays a comparison of the LSD 95% confidence level of the extractives content for the torrefied and the raw sewage sludge. Torrefaction always decreases the extractives content of the solid. Sewage sludge torrefied at 320 °C and 10.2 min shows the biggest reduction in extractives content.

3.3.6. Sulfur removal

Sulfur removal from the solid is an important parameter to study in torrefaction if the torrefied solid is going to be subsequently subjected to pyrolysis. This parameter was calculated as the percentage of S removed by means of torrefaction compared to the amount of S in the raw material fed. S removal did not vary among the different torrefaction conditions studied. The comparison between S content (daf) of the raw material and torrefied sewage sludge showed that torrefaction provoked a decrease in the S content (daf) with respect to the initial content in raw sewage sludge at 320 °C and solid residence time over 6.1 min.

3.4. Torrefaction liquid properties

In view of the fact that TSS could be used in thermochemical processes such as pyrolysis, it is desirable to obtain high yields to water and low yields to organic compounds in the torrefaction step, since pyrolysis oils should have lower water content and higher content in organic compounds. The total water content of torrefaction liquid (condensables) varies from 67 to 99 wt.%.

3.4.1. Water yield

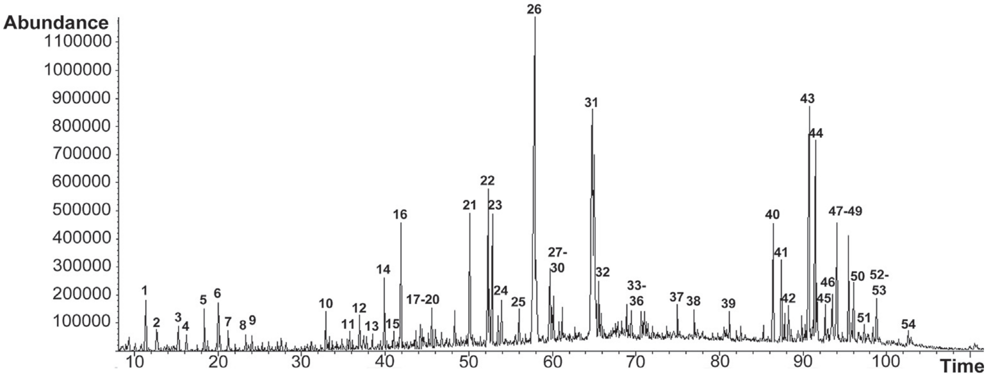
The yield to water ranges from 3.7 ± 1.0 to 15.6 ± 1.0 wt.% in the intervals of the operational conditions under study. This variable, as a function of torrefaction temperature and solid feed rate, is plotted in Fig. 10a.

Similarly to what was observed for other response variables, the water yield increases when temperature augments, especially from 270 to 320 °C, because of kinetic aspects. Table 5 shows that the operational variable which most affects the water yield is the bed temperature (the coefficient of this term is the highest) and that the relative importance of this term is high (89.40%). Solid residence times longer than 3.6 min provoke an increase in the water yield, especially at 320 °C.

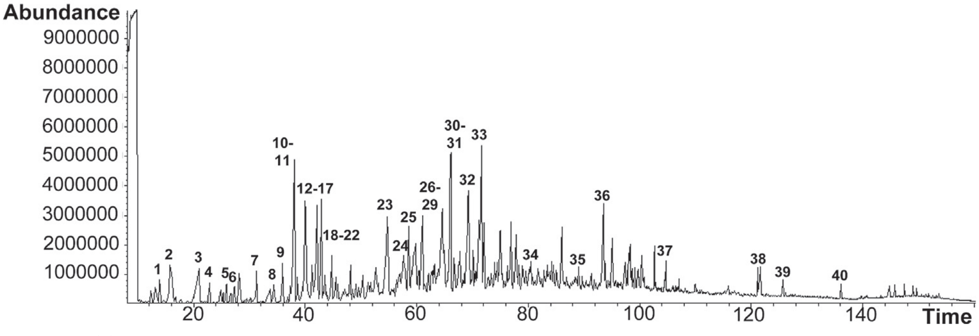
To establish whether the water lost during torrefaction was a result of drying or of other devolatilization processes, the water yield obtained in the torrefaction runs was compared to the initial water content of SS by means of the one-way ANOVA. From Fig. 10b it is apparent that when SS is torrefied at 320 °C and at a solid residence time of 6.1 or 10.2 min the water yield is significantly higher than the initial water content of SS at a confidence level of 95%. In these cases, not only does water evaporation occur during torrefaction but also bound water is removed. Water can be released through organic compounds dehydration reactions.

3.4.2. Organic compounds yield

The yield to organic compounds obtained is very low, in most cases lower than the standard deviation of the results obtained for the liquid yield at the center point conditions. It was thus not possible to carry out a statistical analysis of the results. The organics yield is only noticeable at the most severe torrefaction conditions, at 320 °C and 6.1 or 10.2 min of solid residence time, obtaining 5.4 and 7.6 wt.% respectively, as can be observed in Table 4. Torrefaction liquid from all the experiments separated into two phases, which means that both water and organic compounds were obtained but it was not possible to accurately determine the



(a) 1. Urea, tetramethyl-, **2.** 2-Furanmethanol, **3.** Phenol, **4.** Isosuccinic acid, **5.** Propylamine, **6.** 4-Cresol, **7.** 3-Pyridinol, **8.** Octanoic acid, **9.** 6-methyl-3-Pyridinol, **10.** n-Decanoic acid, **11.** 1-Dodecanol, **12.** 1-Phenyl-3-[bis(methoxycarbonyl)methyl]hex-1-en-4-yne, **13.** Acetylglycine **14.** Indole, **15.** Phencyclidine, **16.** Dodecanoic acid, **17.** 4-Propenylguaiacol **18.** 1-Tetradecanol, **19.** Myristic acid, 2-(1-octadecenyloxy)ethyl ester, (E)-, **20.** Tridecanoic acid, **21.** Tetradecanoic acid, **22.** Pentadecanoic acid, **23.** 1-Hexadecanol, **24.** 9-Tetradecenoic acid, **25.** n-Hexadecanoic acid, **26.** 9-Hexadecenoic acid, **27.** 1-Octadecanol, **28.** 9-Octadecen-1-ol, (E)-, **29.** Heptadecanoic acid, **30.** Stearic acid, 2-(9-octadecenyloxy) ethyl ester, (Z)-, **31.** Octadecanoic acid, **32.** Nonadecanoic acid, **33.** (Z,Z)-,9,12-Octadecadienoic acid, **34.** Decanedioic acid, **35.** Glycerin, **36.** Eicosanoic acid, **37.** Hexadecanoic acid, 2-hydroxy-1,3-propanediyl ester, **38.** Docosanoic acid, **39.** Diisooctyl phthalate, **40.** Cholest-4-ene, **41.** Cholest-3-ene, (5β)-, **42.** Cholestan-3α-ol, **43.** Cholest-2-ene, **44.** A-Norcholestan-3-one, 5-ethenyl-,(5.β.)-, **45.** 14-methyl-5α-Cholest-8-en-3-one, **46**. Urs-12-en-28-al, **47.** Cholestane-3,5-diol, (3β,5α)-, **48.** Cholest-4-ene-3,6-dione, **49.** Stigmastan-3,5-diene, **50.** Methyl (25RS)-3α-hydroxy-5β-cholestan-26-oate, **51.** 2- Chloropropionic acid, hexadecyl ester, **52.** (2α,3α)-Epoxy-(5α)-cholestane, **53.** Stigmasterol, 22,23-dihydro-, **54.** 9,19-Cycloergost-24(28)-en-3-ol, 4,14-dimethyl-, acetate.



(b) 1. Acid thiocyanic, **2.** Hydrogen sulphide, **3.** Glycine, **4.** 4-Methylpentanoic acid, **5.** Hexanoic acid, **6.** Phenol, **7.** Hydroquinone, **8.** Glycoaldehyde, **9.** 3-Methoxyphenol, **10.** Glycerin, **11.** 3-Pyridinol, **12.** 2',3',4' Trimethoxyacetophenone, **13.** 2-(1-Methylethyl)-quinoline, **14.** 6-Methyl-3-pyridinol, **15.** 2-Pyrrolidinone, **16.** 2-Methoxyphenol, **17.** 2,4,6-Trimethoxyacetophenone, **18.** 3-Methyl-1-cyclohexen-1-ol, **19.** 4-Methylpyridine-1-oxide, **20.** Catechol, **21.** (E)-2-Octenoic acid, **22.** 3-Formyl-10-methylphenothiazine, **23.** Resorcinol, **24.** (1R)-(-)-Thiocamphor, **25.** 5-Methylpyrimidine-2,4-diol, **26.** Dihydro-2,4(1H,3H)-pyrimidinedione, **27.** Stearic acid, 2-(1-octadecenyloxy), ethyl ester, (Z)- **28.** Benzenepropanoic acid, **29.** 3-Methyloctadecane, **30.** Heptamethyl-3-phenyl-1,4-cyclohexadiene, **31.** Benzene, 1,1',1''-(butoxymethylidyne) tris-, **32.** 4-methylquinoline, **33.** Phencyclidine, **34.** 2,4-Dichloro-5-nitrobenzotrifluoride, **35.** 3-(4-Hydroxy-3-methoxyphenyl)-1-propanol, **36.** Androst-5,7-dien-3-ol-17-one, acetate, **37.** Triethylene glycol, **38.** 3,6,9,12-Tetraoxa-2,13-disilatetradecane, 2,2,13,13-tetramethyl-, **39.** Emetan, 1',2'-didehydro-6',7',10,11-tetramethoxy-, **40.** Tetraethyleneglycol monomethylether.

Fig. 11. GC/FID chromatograms corresponding to the organic (a) and the aqueous and (b) phases obtained after torrefaction of SS at 320 °C and 11 g min^{-1}.

amount of the latter. In some cases, such a small amount of organic phase was obtained that the perfect separation of this phase was complicated and its characterization was not entirely correct.

3.4.3. Composition

The compounds present in some samples of torrefaction condensable phases were identified using GC–MS. Specifically, the organic and the aqueous phases obtained after torrefaction of sewage sludge at 320 °C and 6.1 min were analyzed. Fig. 11 shows chromatograms of the organic (a) and aqueous (b) phases. The majority compounds present in the organic phase are fatty acids, fatty alcohols, fatty acid esters and steroids, while phenols and fatty acids are the main components of the aqueous phase. As fatty acids, fatty alcohols and steroids are present in the original sewage sludge, it seems that they are not reaction products but compounds that evaporate during torrefaction. Phenolic compounds could come from polysaccharides and proteins reactions [31]. Huang et al. [32] also found some of these compounds in the liquid from rice straw and pennisetum torrefaction and suggested that this liquid could be used to generate heat or electricity, for example by anaerobic digestion, and also as raw material for green chemicals after the appropriate treatments.

3.5. Torrefaction gas properties

The gas product obtained from torrefaction is mainly composed of CO_2, CO, H_2, CH_4, C_2H_4, C_2H_6 and H_2S, depending on the torrefaction conditions. CO_2 and H_2 are always present in the gas product obtained from the torrefaction experiments, whereas the other gaseous compounds are only generated at certain torrefaction conditions. The yield to each one also depends on the torrefaction operational conditions. The carbon dioxide yield (η_{CO2}) and hydrogen sulfide yield (η_{H2S}) were chosen as the most important variables for this product, because if TSS is going to be thermochemically processed it is desirable to eliminate CO_2 and H_2S in the torrefaction step.

These yields were calculated as the ratio between the mass of CO_2 or H_2S and the mass of raw SS introduced for each experiment.

The yield to CO_2 in the torrefaction experiments varies between 0.00 ± 0.10 and 2.41 ± 0.11 wt.%. Fig. 12 shows the effect of T and Q_{feed} on the CO_2 yield. For the three solid feed rates studied, the CO_2 yield is very low and varies slightly from 220 to 270 °C for the whole solid residence time interval studied. However, the CO_2 yield increases as the temperature increases from 270 to 320 °C, especially for 6.1 min and longer solid residence times, reaching values over 2.00 wt.%. When torrefaction is carried out at 320 °C, the carbon dioxide yield decreases from 2.41 ± 0.11 to 0.65 ± 0.11 wt.% as the solid residence time decreases. Decarboxylation reactions begin to be noticeable at temperatures higher than 270 °C and solid residence times longer than 6.1 min. The carbon dioxide yield mainly depends on temperature as can be observed in the model coefficients table (see Table 5).

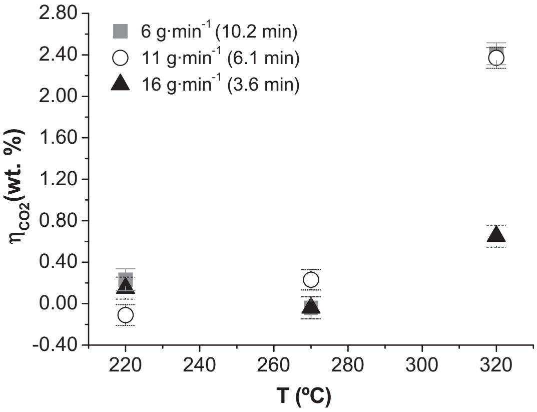


Fig. 12. CO_2 yield vs. temperature for different solid feed rate values. Negative values result from the model adjustment. The results are expressed as the model value at each torrefaction condition ±0.5·Fisher LSD interval (taking into account all the runs).

Table 6
Response variables, objectives, weights, importance and intervals of values obtained.

Response variable	Objective	Weights	Importance	Interval of values obtained
η_{H2O} (wt.%)	Maximize	10	4	4.1–16.0
η_{CO2} (wt.%)	Maximize	5	3	0.02–2.51
η_{energy} (%)	Maximize	8	5	66.7–97.6

Concerning the H_2S yield, the results vary between 0.000 ± 0.010 and 0.297 ± 0.015 wt.% for the conditions under study. The results follow a similar trend to the CO_2 yield, so Fig. 12 also explains the H_2S yield behavior observed in this study. It seems that again the temperature is the parameter that most affects the yield to this product, but the behavior of the H_2S yield with temperature is not the same for all the solid feed rates. While for 3.6 min the H_2S yield hardly changes with temperature, for 6.1 and 10.2 min this yield increases as the temperature increases from 270 to 320 °C, reaching values over 0.25 wt.%. H_2S release is hardly noticeable until temperatures are above 270 °C and the solid residence time is around 6.1 min.

3.6. Theoretical prediction of the appropriate operating conditions within the range of study

To make better thermochemical use of SS, this material should have some specific characteristics in terms of, for example, heating value or oxygen content. It is necessary to find a compromise solution among all the response variables, because the appropriate operational conditions can be different depending on the variable. The operating conditions that could optimize the fuel properties of TSS have been predicted on the basis of the empirical models obtained for the variables studied.

First of all, the response variables to be optimized and the objective for each variable were chosen. If torrefaction is intended to contribute to pyrolysis liquid improvement, it is desirable to obtain high yields to water and to CO_2, and to have high energy yield. Then a weight and degree of importance were assigned to each response variable. The weight (between 1 and 10) is linked to how important it is to achieve the optimum. The importance coefficients (between 1 and 5) make it possible to set priorities among the different response variables. Once the weight and importance coefficients were assigned, a desirability function was built. This function combines the value of the coefficients and the empirical models obtained. It is an objective function which is maximized under particular operating conditions. These conditions were chosen as the more appropriate torrefaction conditions within the range of study. The response variables, objectives, weights and importance selected, together with the intervals of the values obtained are shown in Table 6.

The solution with the highest value of the desirability function predicts that torrefaction should be carried out at 320 °C and 13.0 g min^{-1} (solid residence time around 4.9 min). Under these conditions, the values calculated for water, carbon dioxide and energy yield are 13.8 wt.%, 1.89 wt.% and 84%, respectively. However, the maximum reached for the desirability function is very low (0.049). Therefore, it is difficult to reach a compromise between high energy yield and high water yield.

4. Conclusions

The influence of sewage sludge torrefaction operational conditions (temperature and solid residence time varied by means of solid feed rate) on product distribution and some properties of these products has been studied by means of an experimental design, concretely a Central Composite Design. SS torrefaction experiments performed in a lab-scale fluidized bed has made it possible to draw the following conclusions:

Temperature and solid residence time in SS torrefaction pretreatment hardly affect the response variables studied at temperatures lower than 270 °C and solid residence times below 10.2 min. However, temperature influences the response variables from 270 to 320 °C for longer solid residence times analyzed (6.1 and 10.2 min). At these conditions, the TSS yield decreases with increasing temperature whereas the yields of condensable vapors and permanent gases increase. Besides, the water yield is higher than the initial water content of sewage sludge. In these cases, bound water is released during the torrefaction experiments. Solid residence time has its main effect at the highest temperature of the interval studied. According to the results obtained for the CO_2 yield, increasing torrefaction temperature increases this gas yield, also for short residence times. At 320 °C and solid residence times of 6.1 and 10.2 min torrefied sewage sludge has a considerably lower O/C ratio than raw sewage sludge, which could entail the reduction of the oxygen content of torrefied sewage sludge pyrolysis liquid.

It can be concluded from the results of this work that the higher heating values and daf higher heating values of TSS are higher than the higher heating value of raw SS when torrefaction is carried out under certain operational conditions, although energy density is slightly influenced by torrefaction. Also at 320 °C and solid residence times of 6.1 and 10.2 min, the energy yield is below 95. 0% (values below 80.0% and 70.0% respectively). Under the most severe torrefaction conditions, devolatilization reactions give rise to the release of a large amount of compounds, which results in a massive torrefied sewage sludge yield reduction and therefore in the energy yield reduction, although the higher heating value (daf) increases.

The results obtained would seem to indicate that values of solid residence time below 10.2 min and a temperature over 270 °C are needed at the torrefaction stage in order to appreciate important effects on the thermochemical behavior of sewage sludge. The choice of the most appropriate operational conditions in the torrefaction pre-treatment in order to improve the subsequent pyrolysis liquid requires a particular study on pyrolysis of torrefied SS. The results obtained in the present work should be corroborated by comparing the pyrolysis of sewage sludge both with and without torrefaction.

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